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# Raney Nickel–Copper Catalysts

## I. Structure and Leaching Properties

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The leaching behavior in aqueous NaOH of Al–Cu–Ni alloys containing 50 wt% Al has been examined and interpreted in terms of alloy phase constitution. The alloys contained approximately 0, 10, 20, 30, 40, and 50 wt% Cu and had quenched structures consistent with the ternary phase diagram. The alloys were partly leached and the product was examined metallographically. The Al–Ni alloy leached rapidly, the relative reactivity of the phases being Al(Ni) > $NiAl_3$ > $Ni_2Al_3$. The addition of Cu greatly decreased the leachability of the solid solution phase $(Ni, Cu)_2Al_3$. At high Cu levels the ternary phase $Cu_4NiAl_7$ appeared and was found to be resistant to leachant attack. The ternary alloys all had leaching kinetics of the protective type in which a limiting depth of attack was approached. The binary Al–Cu alloy behaved similarly whereas the binary Al–Ni leached rapidly to completion.

## INTRODUCTION

Nickel catalysts, including Raney nickel, are of great practical importance in the production of substitute natural gas from coal (*1*) via the methanation reaction. Recently there have been several studies on the use of nickel–copper alloy catalysts for both methanation (*2*) and Fischer–Tropsch synthesis (*3*). In these studies the effect of the inclusion of copper has been examined to elucidate the mechanism of these two important reactions (*4*). The addition of copper strongly reduces the rates of both reactions relative to pure nickel catalysts. In methanation at low pressures (2) the addition of 10% Cu to a nickel film decreased the activity to a low value.

A part of the activity changes of Raney nickel produced by adding Cu has been attributed to modifications of the phase composition of the initial alloy that alter the extent of leaching (*5–7*). Reynolds (*8*) has made a detailed study of hydrogenation reactions using Raney Ni–Cu catalysts and has attributed the decreased activity to the filling of holes in the 3*d*-band of nickel by the valence electrons of copper.

In none of the studies on Raney Ni–Cu was any attempt made to follow the extent or rate of leaching. The present paper provides new information on the leachability of the various phases in the Ni–Cu–Al system by a systematic study using metallographic, X-ray diffraction, and electron microprobe methods of analysis.

## METHODS

### *Catalyst Preparation*

Samples of the alloys listed in Table 1 were obtained as 8-mm pieces from the Davison Chemical Division of the W. R.

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[1] This work was initiated while M. S. Wainwright was on sabbatical leave at McMaster University.

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TABLE 1

Compositions and Extent of Leaching of Alloys

| Sample | Alloy (wt%) | | | Catalyst (wt%) | | | Al extraction (%) | |
|---|---|---|---|---|---|---|---|---|
| | Ni | Cu | Al | Ni | Cu | Al | $H_2$ evolution | AAS analysis |
| 1 | 41.2 | 0.06 | 59.3 | 81.0 | 0.15 | 11.8 | 85.3 | 89.9 |
| 2 | 38.4 | 10.8 | 51.8 | 50.7 | 14.2 | 32.9 | 52.4 | 51.8 |
| 3 | 29.0 | 20.5 | 49.1 | 34.2 | 23.6 | 44.1 | 28.9 | 23.1 |
| 4 | 21.1 | 29.2 | 50.8 | 25.5 | 37.0 | 39.9 | 40.5 | 36.8 |
| 5 | 9.4 | 39.2 | 53.2 | 14.3 | 59.6 | 27.9 | 67.8 | 65.5 |
| 6 | — | 49.0 | 52.4 | — | 97.4 | 1.9 | 98.3 | 98.2 |

Grace Company, courtesy of S. R. Montgomery.

Catalysts were prepared by a procedure similar to method II described by Freel and co-workers for Raney nickel (9). Alloy samples were crushed and screened, and particles having diameters between 300 and 500 μm were reacted with aqueous NaOH at 40°C after first purging with nitrogen.

Forty percent aqueous NaOH, 150 ml, was added stepwise to 30 g of alloy in 150 ml of distilled water. Alkali additions were made at 2-min intervals. Volumes of 2 ml were added over the first 20-min period and 5-ml additions were made thereafter. Reaction was allowed to proceed for 3 h after which the extracted catalysts were washed with distilled water at 25°C, first by decantation and finally by water flow in a stirred vessel until the pH of the wash water was 7. The samples were stored under deaerated distilled water in stoppered vessels prior to use.

The extent of oxidation of Al was measured by monitoring the evolution of hydrogen as a function of time with a wet test meter. Another measure of alkali attack, the fraction of the Al removed from the alloy, was calculated from the compositions of the alloy and the extracted material. These quantitites should be the same if all of the Al oxidized is dissolved in the aqueous caustic. The alloys and leached materials were dissolved in acid and analyzed by atomic absorption spectroscopy.

Large specimens for use in electron microprobe and metallographic analyses were prepared by leaching in test tubes immersed in a water bath with caustic additions in the same proportions as described above. No means for hydrogen monitoring and stirring were provided.

### *Morphological Investigations*

Partly extracted alloy pieces were mounted in cold setting resin, cross sectioned, and polished to a 0.5-μm finish. To measure the depth of chemical attack on an alloy, it is desirable to examine a cross section in a plane parallel to the direction of attack. The alloy pieces being examined here were so irregular in shape that a single, randomly chosen cross section was assumed to contain an unbiased sampling of angles to the original alloy surfaces, and hence to the direction of attack. The reaction-affected rim of the alloy piece was clearly visible under an optical microscope, and its thickness was measured with a graduated eyepiece.

### *Phase Identification*

Phases present in the unaffected alloy and in the reacted rim were analyzed with an electron microprobe. Point counts obtained from the probe were calibrated with $CuAl_2$, $NiAl_3$, and Al standards. Systematic corrections were applied to the data for atomic number, mass absorption, and fluorescence effects.

Microprobe results were supplemented by powder X-ray diffraction studies. Samples of powdered unreacted alloys were examined with a diffractometer in the usual way. After extraction, the powdered catalysts were pyrophoric and were therefore coated with Collodion prior to examination. In both cases Cu$K_\alpha$ radiation was used and phase identification was accomplished by comparing diffraction patterns with those in the ASTM files and, in the case of the ternary phase $Cu_4NiAl_7$, the pattern reported by Lu and Chang (*10*).

## RESULTS

### *Rates and Extent of Leaching*

The curves of cumulative hydrogen evolution are shown in Fig. 1. The extent of aluminium extraction was calculated from the volume of $H_2$ on the basis of only the aluminum being oxidized and removed from the alloy. Similar calculations were made on the basis of chemical analysis of the alloys before and after leaching. These results are presented in Table 1 and indicate good agreement between the two methods of calculation. The thickness of the reaction-affected rim around the partially extracted alloy pieces is shown as a function of time in Fig. 2.

### *Reaction Morphology and Phase Constitution*

In all cases a clearly defined boundary was found to exist between a reaction product zone and the underlying, as yet unaffected, alloy. Micrographs in Fig. 3 show this interface, or reaction front, for each of the alloys. Microprobe analyses for each of the phases seen in the micrographs are listed in Table 2.

Phases identified by X-ray diffraction for the alloys and their catalyst products are shown in Table 3. Microprobe scans showed that no concentration gradients existed in any of the phases and that within the spatial resolution of the technique (±2 μm) a discontinuous change in concentration occurs (in phases undergoing leaching) at the reaction front. Analyses of the dark phases in the reaction product zone were found to total substantially less than 100%, indicating either that oxide is present or that the analysis of these porous materials is unreliable. The chemical analyses shown

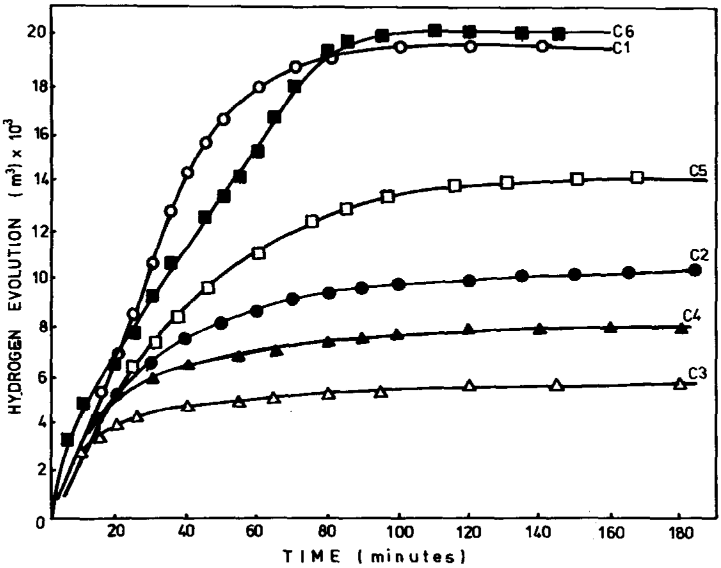

FIG. 1. Cumulative hydrogen evolution from alloy particles 300–500 μm in aqueous NaOH as a function of time.

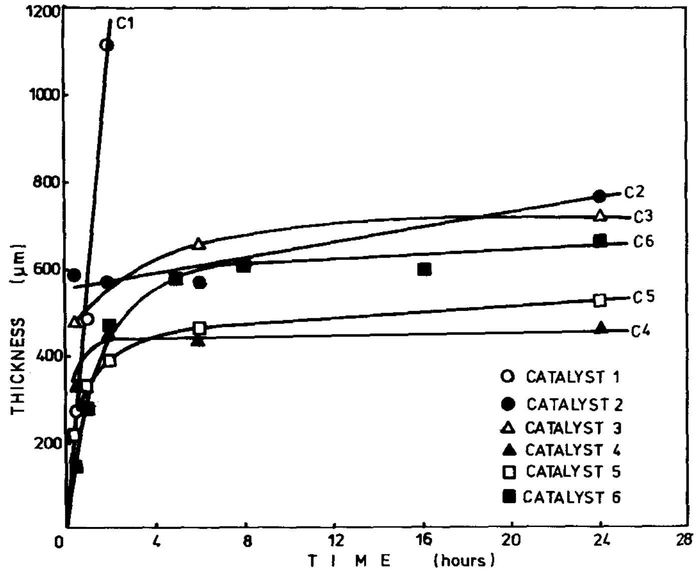

FIG. 2. Average thickness of reaction-affected rim as a function of leaching time.

in Table 1 indicate that, with the exception of the Ni–Al alloy, the oxide hypothesis is untenable.

## DISCUSSION

### *Alloy Structures*

Microprobe and X-ray diffraction (XRD) results for the alloys are mutually consistent except for alloys 4 and 5 wherein the ternary phase $Cu_4NiAl_7$ detected by XRD could not be distinguished with the microprobe. Lu and Chang (*10*) report $Cu_4NiAl_7$ compositions ranging between $Ni_9Cu_{29}Al_{61}$ and $Ni_{12}Cu_{26}Al_{62}$ which are close to the composition range of $(Ni, Cu)_2Al_3$. If, as discussed below, the phases are formed in intimate association, it is not

TABLE 2

Microprobe Analyses of Alloys and Their Product Raney Catalysts

| Sample | Alloy | | Catalyst | |
|---|---|---|---|---|
| 1 | Gray precipitate | $Ni_{39}Al_{61}$ | Gray phase | $Ni_{39}Al_{61}$ |
| | Light matrix | $Ni_{25}Al_{75}$ | Dark phase[a] | $Ni_{82}Al_{18}$ |
| | Liquid | $Ni_1Al_{99}$ | Black region | Void |
| 2 | Gray phase | $Ni_{34}Cu_7Al_{59}$ | Gray phase | $Ni_{31}Cu_6Al_{60}$ |
| | Light phase | $Ni_{23}Cu_1Al_{75}$ | Dark phase[a] | $Ni_{94}Cu_4Al_2$ |
| | Liquid | $Ni_1Cu_1Al_{98}$ | Black region | Void |
| 3 | Gray phase | $Ni_{31}Cu_{10}Al_{59}$ | Gray phase | $Ni_{32}Cu_8Al_{59}$ |
| | Liquid | $Ni_1Cu_1Al_{97}$ | Black region | Void |
| 4 | Gray needles | $Ni_{27}Cu_{15}Al_{58}$ | Gray needles | $Ni_{28}Cu_{12}Al_{60}$ |
| | Matrix | $Ni_1Cu_{15}Al_{84}$ | Black region | Void |
| 5 | Gray needles | $Ni_{22}Cu_{18}Al_{60}$ | Gray needles | $Ni_{23}Cu_{18}Al_{59}$ |
| | Matrix | $Ni_1Cu_{32}Al_{67}$ | Dark gray phase[a] | $Ni_1Cu_{63}Al_{36}$ |
| | Liquid | $Cu_6Al_{94}$ | Black region | Void |
| 6 | Light precipitate | $Cu_{32}Al_{68}$ | Gray phase[a] | $Cu_{97}Al_3$ |
| | Liquid | $Cu_{19}Al_{81}$ | Black region | Void |

[a] Analyses total less than 100% and have been scaled up.

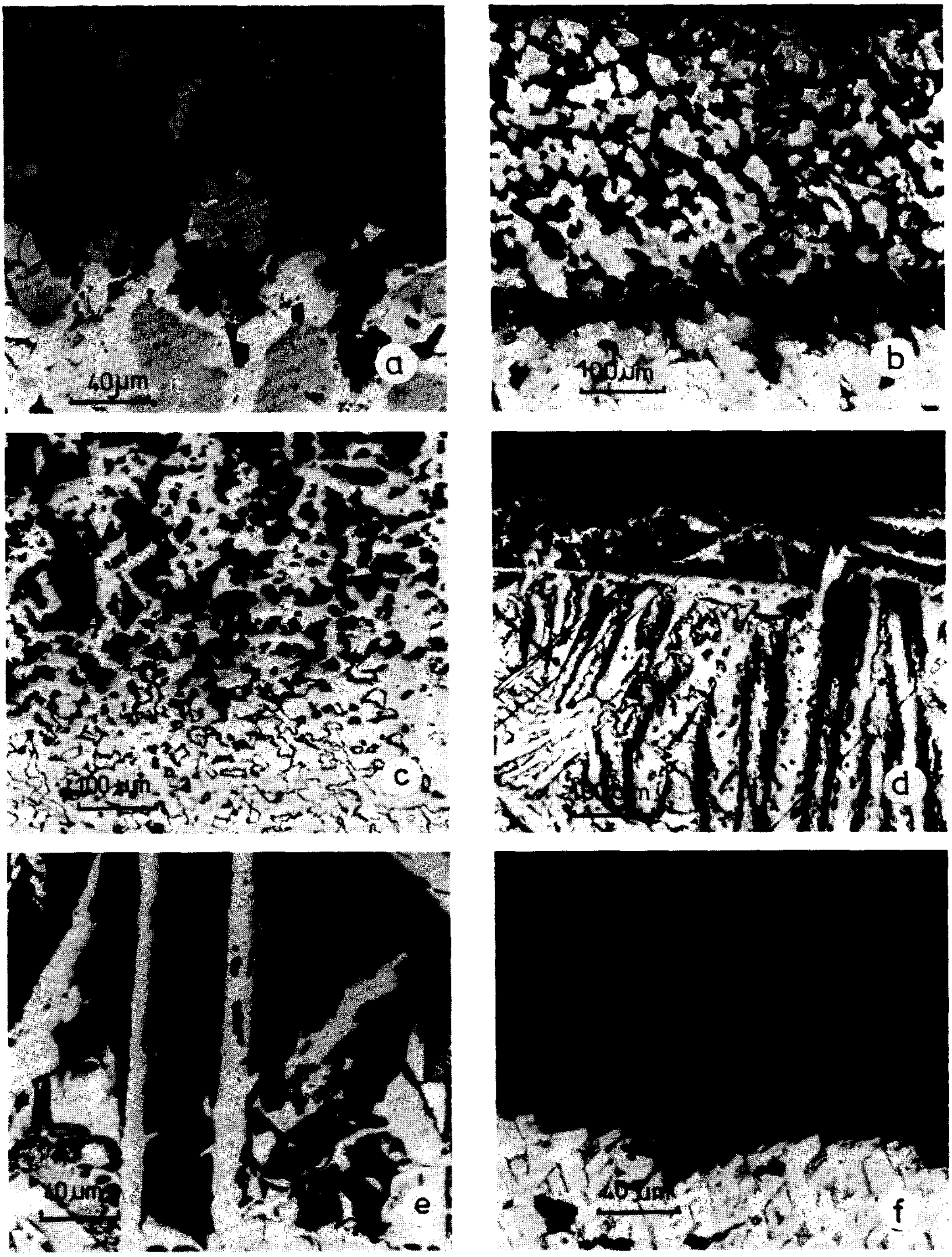

FIG. 3. Micrographs of sections through partially leached alloys: (a) Al–41Ni; (b) Al–38Ni–11Cu; (c) Al–29Ni–20Cu; (d) Al–21Ni–29Cu; (e) Al–9Ni–39Cu; (f) Al–49Cu.

surprising that they should not be resolved.

The alloy microstructures are consistent with predictions for quenched alloys made from the liquidus projection diagram (Fig.

TABLE 3

X-Ray Diffraction Analyses of Alloys and Their Product Raney Catalysts[a]

| Sample | Alloy | Catalyst |
|---|---|---|
| 1 | $Ni_2Al_3$,$NiAl_3$,Al(tr) | Ni |
| 2 | $Ni_2Al_3$,$NiAl_3$,Al(tr) | $Ni_2Al_3$,Ni |
| 3 | $Ni_2Al_3$,Al | $Ni_2Al_3$,Ni(tr) |
| 4 | $Ni_2Al_3$,$Cu_4NiAl_7$,Al(tr) | $Ni_2Al_3$,$Cu_4NiAl_7$,Ni(tr) |
| 5 | $Cu_4NiAl_7$,$CuAl_2$,$Ni_2Al_3$,Al | $Ni_2Al_3$,$Cu_4NiAl_7$,$Cu_2O$ |
| 6 | $CuAl_2$,Al(tr) | Cu,$Cu_2O$ |

[a] Phases listed in approximate order of abundance; (tr) indicates trace.

4) where the compositions of the alloys and their primary precipitates are shown. Thus alloys 1–5 have as their primary precipitate the phase (Ni, $Cu)_2Al_3$, the Cu content of the precipitate increasing with alloy Cu level. In the case of alloy 6, the primary precipitate is $CuAl_2$. The identity of the secondary precipitate in alloys 1 to 5 is determined by the alloy Cu level: alloys 1 and 2 precipitate $NiAl_3$; alloy 3 precipitates Al; alloys 4 and 5 precipitate $Cu_4NiAl_7$. On further cooling the Al-based solution is the final solidification product in alloys 1 and 2; no further solidification products are detected in alloy 3; alloy 4 produces a solid of composition approximating that of the ternary eutectic mixture but individual phases are not distinguishable; alloy 5 also reaches the ternary eutectic composition and in this case all three solids are detected by XRD, and both $CuAl_2$ and the Al solid solution are resolved by the microprobe. Alloy 6 produces as its secondary solidification product material of the composition of the binary Al–$CuAl_2$ eutectic.

### *Morphology of Leaching*

Examination of Fig. 3 together with the phase identifications shown in Tables 2 and 3 reveals the relative leachabilities of the different phases. In agreement with Freel *et al.* (*11*) we find that in the binary Ni–Al, alloy 1, the order of rapidity of leaching is Al(Ni) > $NiAl_3$ > $Ni_2Al_3$, the Al solid solution leaving void space upon leaching. The $Ni_2Al_3$ precipitates are still visible in the reacted rim near the reaction front but have almost disappeared at the outer surface where the time of exposure to the leach solution has been greatest. Alloy 2 which has a closely similar microstructure again shows rapid leaching of Al to yield voids and rapid leaching of $NiAl_3$ to yield porous catalyst but apparently complete immunity of the (Ni, $Cu)_2Al_3$ phase to leachant attack. This finding is consistent with those of the Russian workers (*5*, *6*).

The resistance of the copper-enriched (Ni, $Cu)_2Al_3$ to alkali attack is seen in all cases where the phase exists (alloys 2–5). However, the behavior of the secondary phases varies considerably. In alloy 3 the high Al phase leaches completely to leave void space and no other reaction is seen. In alloy 4 the matrix (of eutectic composition) leaches to yield void space. In alloy 5 where a separate $CuAl_2$ phase exists, porous Cu is found as a leach product. The Al phase in this alloy leaches completely to leave a void space. The $Cu_4NiAl_7$ phase is detected by XRD in the catalysts derived from alloys 4 and 5. Since no $CuAl_2$ is detected in the catalyst formed from alloy 5, presumably no remnant, unaffected alloy is present and it can be concluded that $Cu_4NiAl_7$ is resistant to leaching.

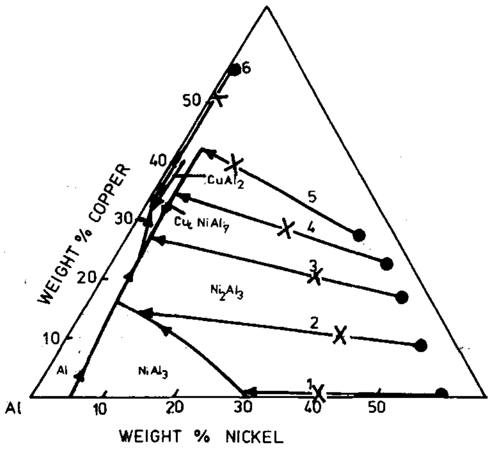

FIG. 4. Liquidus projection (*14*) for the system Al–Ni–Cu showing the average compositions of the initial alloys (X) and their primary precipitates (●).

Leaching of alloy 6 leads to the formation of porous Cu from $CuAl_2$ and to void space from the eutectic material, the microstructure of the alloy being reproduced in the catalyst. The similarity in appearance of the porous Cu formed from alloys 6 and 5 indicates that the porous Cu in the latter was indeed derived from the $CuAl_2$ phase.

### *Rates and Extent of Leaching*

The data obtained on rates and extent of leaching of the 300- to 500-μm particles (Table 1 and Fig. 1) are consistent with the metallographic measurements of larger pieces leached for various periods of time. However, there is some difference between the thickness of the reaction-affected rim for Catalyst 6 (Raney Cu) and what might be expected from the studies on the finer particles. It can be seen from Fig. 1 that the rate of extraction is negligible after a period of approximately 2 h and from Table 1 that essentially all leachable aluminum had been removed from the samples when they were washed free of alkali after a period of 3 h.

The chemical analyses of all catalysts except Sample 1 (Raney Ni) gave excellent material balances. The shortfall of around 7% for that catalyst can be attributed to the large amount of alumina trihydrate which is formed by the extraction procedure (*9*). It is evident that very little alumina is present in the other catalysts including Raney Cu which was leached almost quantitatively. The extent of aluminum extraction is consistent with the data of Reynolds who studied a similar range of alloys on smaller particles (less than 75 μm in diameter).

Metallographic investigation of the leaching reaction has provided data which are consistent with the other methods of analysis used in this work except in the case of Catalyst 6 (Raney Cu). An 8-mm piece of Raney Ni alloy was completely extracted after a period of less than 4 h. The mixed Cu–Ni alloys underwent rapid extraction initially but reaction became negligible after a period of about 2 h corresponding to a reaction rim thickness of between 450 and 720 μm. The poor extraction of these catalysts might be explained by the presence of unextractable phases in the extracted layer limiting access of the leach liquor to the catalyst–alloy interface; the process is possibly diffusion limited. Such an argument is difficult to apply to Raney Cu which when in the form of a 300 to 500-μm powder extracted almost quantitatively to yield a highly porous catalyst of almost pure Cu, but which in the form of large pieces experienced an almost complete cessation in reaction after a reaction rim of about 600 μm was formed. In a subsequent paper (*12*) we show that this catalyst has large pores (around 0.10 μm in diameter) and a BET surface area of approximately 15 $m^2$ $g^{-1}$. Therefore access of the extracting solution would not be expected to be limited by diffusion, particularly when one considers the ease with which Raney Ni is fully extracted under similar conditions.

No explanation of the unusual leaching behavior of alloy 6 can be given on the basis of the experiments conducted. However, considering the recent industrial importance of Raney Cu in the catalytic production of acrylamide and certain patent claims (*13*) on the value of partial extraction of Cu–Al alloys this would appear to be an important field of research.

It has been shown that the nature of Raney Ni–Cu catalysts is determined by the phase constitution of their precursor alloys. The extent of leaching and the nature of the leach product are both determined by the identity of the phases and their relative abundance in the alloy. The consequent effects on catalyst properties will be explained in a subsequent paper (*12*).

## ACKNOWLEDGMENTS

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